感應耦合電漿光譜分析儀在土壤速測之應用

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感應耦合電漿光譜分析儀（Inductively Coupled Argon Plasma Spectrometer-ICAP）是原子發射光譜（Atomic Emission）分析法之一種，具有快速,靈敏及多元素同時分析的特性，因此被作爲多種元素，特別是微量元素分析的主要方法。ICAP利用氬氣電漿激發源，大大提高了原子激發效率，導致測試元素的增加，靈敏度提高及干擾效應的減少，配合新近光譜分析儀的改良和電腦化自動控制及資料處理系統的導入，加上其原有可同時分析多元素的特性，提高了在分析方法中的地位。

ICAP對各種元素的偵測極限，一般可達 ppb或 ppb以下，而且在單一分析條件下，ICAP可同時測定試樣中之主成分，少量成分及微量成分。這是一般分析方法沒有的特點。同時其校正曲線的線性關係特長，可從ppb至%的範圍，且化學干擾和光譜干擾少，穩定性良好，亦少有污染機會。因此用於土壤、植體、水質、飼料、肥料、食品及其他有毒物質的分析，可顯著提高分析速率與品質。

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The Application of Inductively Coupled Argon Plasma Spectrometer in Soil testing

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I. Introduction

Two major advances in technology are changing traditional approaches to nutritional research and fertility management.Sophisticated analytical equipment and microcomputer availability now allow nutritional analysis and diagnostic services that were once logistically and economically unfeasible. With new instrument and data process technique, simultaneous analysis of multielement is possible and time saving.

II. Materials and Methods

1. Soil Samples
   (1) 50 representative soil samples of Taiwan were collected. These samples include latosols, calcareous soils, Taiwan clay, sand and shale alluvial soils, slate alluvial soils and schist alluvial soils.
   (2) Soil samples were collected from Georgia. The cultivated crops were corn, grape, bluecherry,cherry,cucumber,tomato,snapbean, peach,pecan and apple. Lakeland sand,345 front and three reference soil samples were also taken to compare the correlations among different extraction methods of nutrient contents.
2. Methods of Extration
   (1) Determination of P by Bray No.1 extraction

   Bray P1:

   Weigh 2.85 g soil into extraction flask
   Add 20 ml Bray P1 extraction reagent
   Shake for 40 seconds

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Filter and save the filtrate

(2) Determination of P by Bray No.2 extraction

Bray P2:

Weigh 2.85 g soil into extraction flask

Add 20 ml Bray P2 extraction reagent

Shake for 40 seconds

Filter and save the filtrate

(3) Determination of P by Olsen's extraction

Olsen P:

Weigh 5 g soil into extraction flask

Add 100 ml Olsen extraction reagent

Shake for 30 minutes

Filter and save the filtrate

(4) Determination of K, Ca, Mg and Na by 1N pH 7.0 NH_4 OAc extraction

Neutral Normal Ammonium Acetate (NH_4 OAc, pH 7.0):

Weigh 5 g soil into extraction flask

Add 50 ml Ammonium Acetate extraction reagent

Shake for 5 minutes

Filter and save the filtrate

(5) Determination of K,Ca,Mg and Na by Mehlich No.1 extraction

Mehlich No.1:

Weigh 5 g soil into extraction flask

Add 50 ml Mehlich No.1 extraction reagent

Shake for 5 minutes

Filter and save the filtrate

(6) Determination of P,Ca,Mg,K,Na,Mn,Zn and Cu by Mehlich No.3 extraction

Mehlich No.3:

Weigh 5 g soil into extraction flask

Add 50 ml Mehlich No.3 extraction reagent

Shake for 5 minutes

Filter and save the filtrate

(7) Determination of K,P,Zn,Fe,Mn and Cu by AB-DTPA extraction

Ammonium Bicarbonate-DTPA (AB-DTPA):

Weigh 5 g soil into extraction flask

Add 50 ml AB-DTPA extraction reagent

Shake for 15 minutes

Filter and save the filtrate

Add 0.25 ml HNO_3 for each 2 ml of filtrate

3. Extraction Reagents

Bray No.1 extractant - - - 0.025N HCl + 0.03N NH_4 F

Bray No.2 extractant - - - 0.1N HCl + 0.03N NH_4 F

Mehlich No.1 extractant - -0.05N HCl + 0.025N H_2 SO_4

Olsen's extractant - - - - 0.5 M , pH 8.5 $NaHCO_3$

AB-DTPA - - - - - - - - -AB-Diethylenetriamine pentaacetic acid

Mehlich No.3 extractant - -0.2N CH_3 COOH + 0.25N NH_4 NO_3 + 0.015N NH_4 F + 0.013N HNO_3 + 0.001N EDTA

III. Results and Discussions

1. ICAP is a powerful multielement analytical procedure that is fast and cost-effective.
2. The results of the soil samples collected from Georgia indicated that extractable P of Bray No.1 andMehlich No.3 extractants were highly correlated.
3. The contents of soil exchangeable K, Ca and Mg and Mehlich No.3 extraction were linearly correlated.
4. Extractable Mn and Zn by Mehlich No.1 extraction were also linearly correlated with that of Mehlich No.3 extraction, respectively.
5. The correlations of the nutrient contents in the representative soil samples collected from Taiwan by different extraction methods were shown in the following table.

Table. Relationship between different extraction methods of major elements in Taiwan soils

element	extraction (Y)	method (X)	equation	r
P	Bray No.1	Mehlich No.3	Y= -4.15 + 0.77X	0.9317
"	Bray No.2	"	Y= 34.55 + 1.38X	0.6622
"	Olsen	"	Y= 12.30 + 0.43X	0.8314
"	Bray No.1	AB-DTPA	Y= -8.23 + 0.64X	0.8801
"	Bray No.2	"	Y= 11.76 + 1.35X	0.7382
"	Olsen	"	Y= 6.81 + 0.40X	0.8804
K	Ammo.Acet.	Mehlich No.3	Y= 7.68 + 0.86X	0.9921
"	"	Mehlich No.1	Y= -5.20 + 1.19X	0.9083
"	"	AB-DTPA	Y= 11.25 + 1.08X	0.9937
"	Mehlich No.1	Mehlich No.3	Y= 20.57 + 0.61X	0.9368
"	"	AB-DTPA	Y= 26.39 + 0.73X	0.8840
Ca	Ammo.Acet.	Mehlich No.3	Y=593.77 + 0.39X	0.9239
"	"	Mehlich No.1	Y=446.72 + 0.35X	0.9358
"	Mehlich No.1	Mehlich No.3	Y=565.08 + 1.05X	0.9348
Mg	Ammo.Acet.	"	Y= -0.80 + 0.71X	0.9800
"	"	Mehlich No.1	Y= 18.37 + 0.68X	0.8845
"	Mehlich No.1	Mehlich No.3	Y= 15.64 + 0.89X	0.9365

Remarks: 1.Number of observations = 50

2. All relationships significant at 99.9% level

IV. References

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附 錄：
感應耦合電漿光譜分析儀簡介
(Inductively Coupled Argon Plasma Spectrometer)
ICAP-AES 之構造

1. 電漿的形成

ICAP 分析儀一般採用 Fassel等人設計，圖1是典型的ICAP 激發源。通入的三道氣流--輔助氬氣氣流，氬氣電漿支持氣流(Support flow)和載送氣流 (Carrier gas flow)。利用同心的石英管來分隔，最外層石英管的出口處圍繞有感應線圈，線圈連接高頻產生器，產生高至 2.5 kW的輸送功率，在電流(I)的感應下形成振盪磁場 (H)。磁場的磁强和方向作週期性的改變，因而使磁場感應生成的電子流受到加速作用而增加動能。此動能在碰撞中以高熱形式傳遞，而產生加成離子化現象(Additional ionization)，最後形成高熱的電漿。

一般的操作條件是支持氣流流速 15-20 l/min，輔助氣流流速 0.5 l/m (水溶液)，1.5-2.0 l/m(有機物)，載送氣流流速 0.6 l/m 。

圖 1 感應藕合電漿激發源的典型圖示

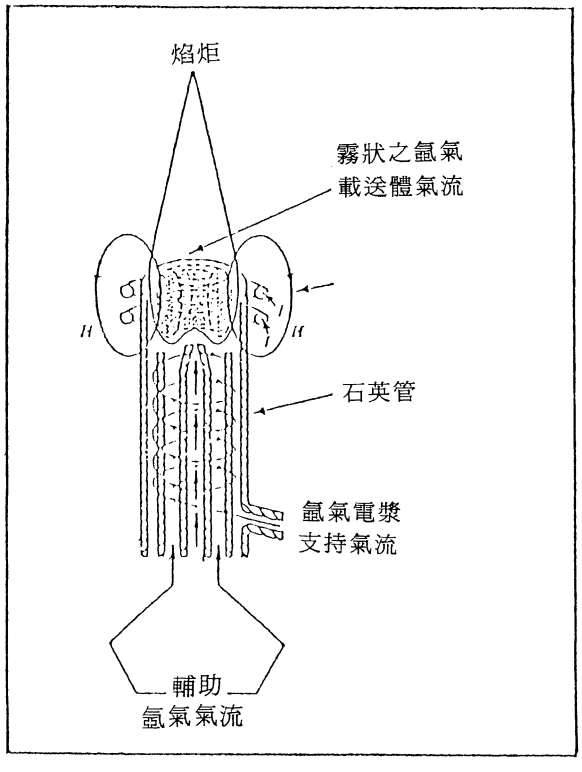
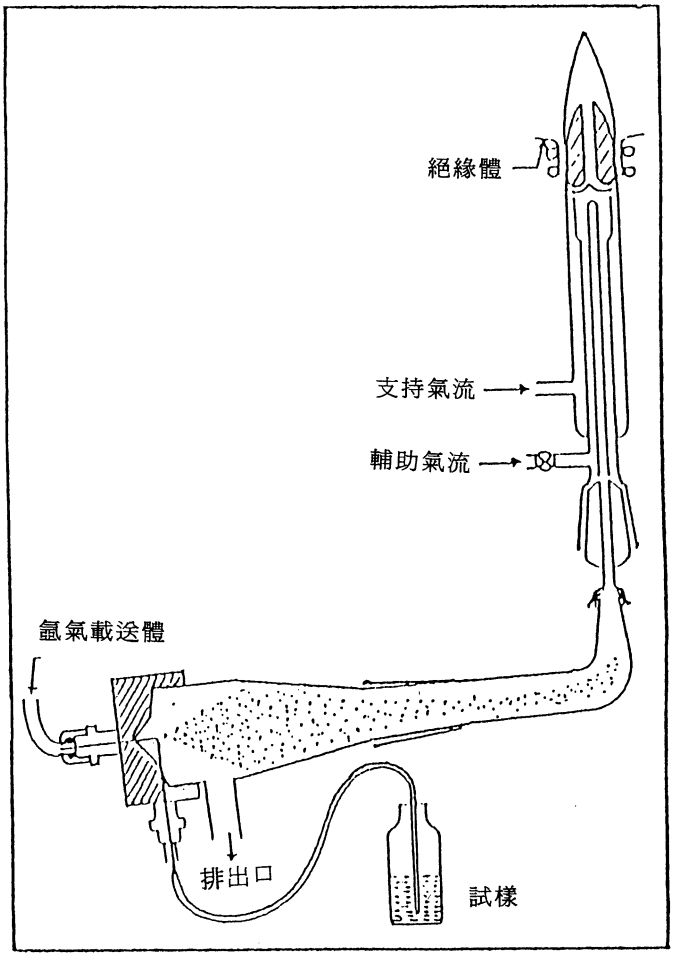


圖 2是輔助氬氣氣流和支持氣流受感應生成電漿的形狀。電漿受支持氣流的作用，集中在石英管管徑範圍內。水氣狀的試樣，經霧化器導入，通過電漿中央，在溫度約7000-8000° k間，試樣氣化，分解。當分解產物到達可測試的高度（高於線圈 15-20 mm)之前，溫度在約 2微秒的停駐時間內，自8000° K降至約 5500° K 。此溫度範圍內，使試樣完全氣化並提高原子化效率。由於此無化學性的氬氣電漿環境下，化學干擾小，加加上原子化的元素集中在狹窄的電漿中央位置，存在時間長，使發射光譜的分析靈敏度增强，發揮最佳的分析效果。

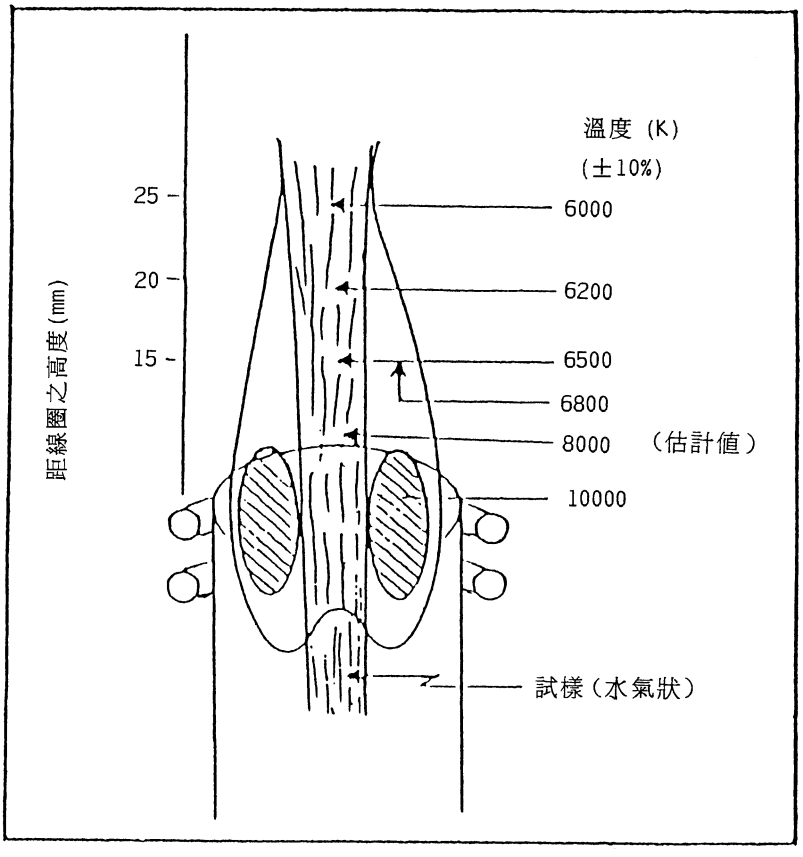
圖 2　氣腔式霧化器 (Pneumatic nebulizer) 屬於交叉氣流式霧化器



2. 試樣的導入

試樣經由氣腔式 (Pneumatic) 霧化器霧化成水氣狀物質(圖 3)，由氬氣載送氣流將其導入電漿焰炬中央激發。

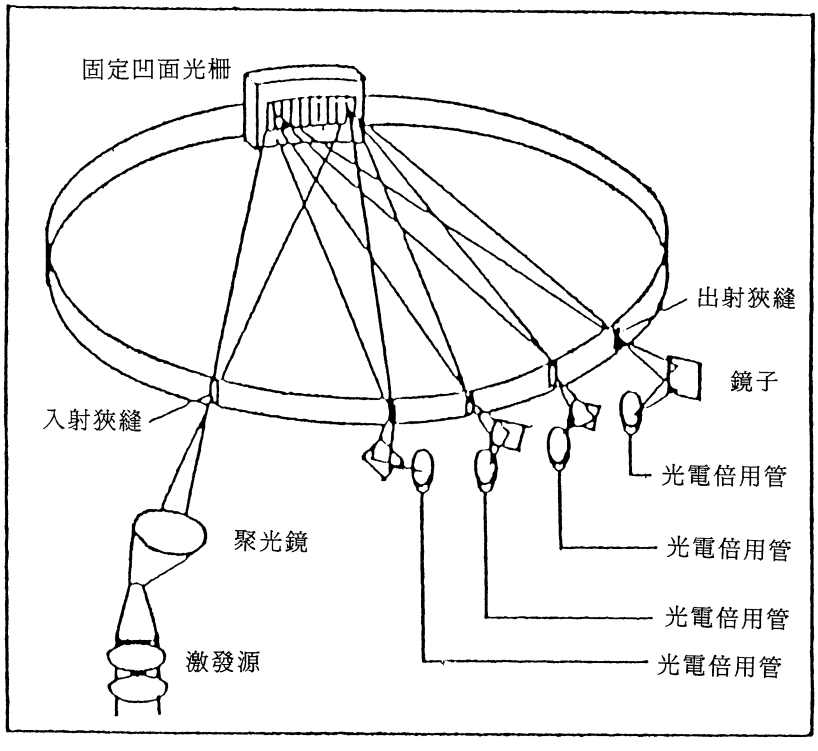
圖 3　感應藕合電漿激發源的溫度分佈情形



3．光譜測定系統

同時式光譜儀（圖 4）：入射的發射譜線經由固定的凹面光柵(Fixed concave-grating)的作用反射至各特性譜線的出射狹縫，再經由各光電倍增管(Photomultiplier)偵測並輸送强度資料，經由內部標準計算，由記錄器記錄分析所得的各元素含量。其優點是由於光柵和特性譜線出射口均爲固定，每一出射狹縫均有一個光電倍增管偵測出射譜線，可同時偵測試樣中的各元素含量，且可提供較高的精確度，對於固定數目的元素分析效果良好。

圖 4　同時測定式光柵光譜儀的構造

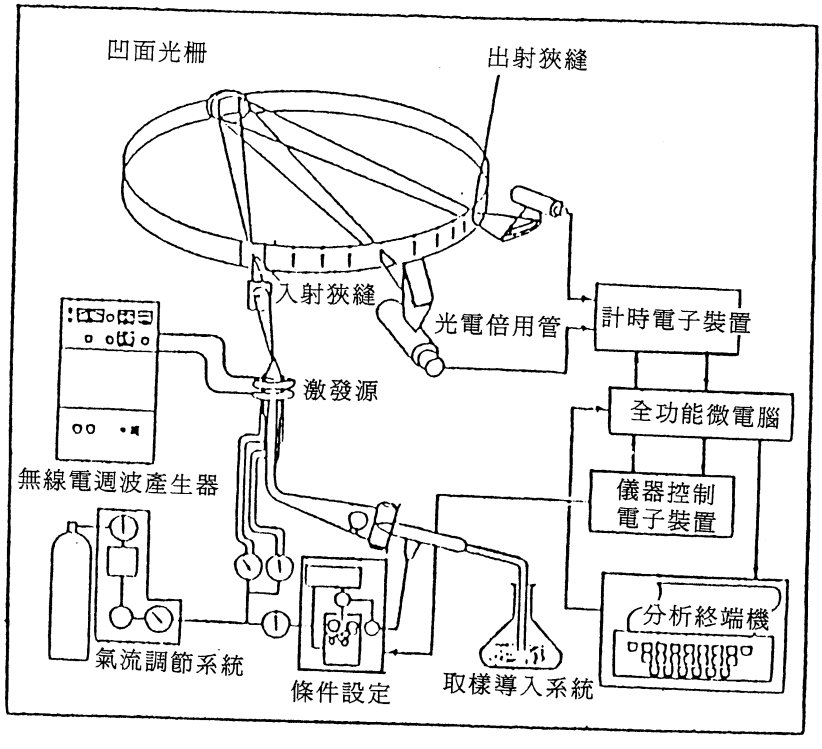


4．資料處理系統

經由光電倍增管轉化傳送的譜線强度資料輸入電子系統後，藉微電腦的分析處理，從終端機傳遞出分析結果。由於電腦的功能，不僅加快分析資料的獲得，也使儀器的自動校正精密準確，降低系統誤差的導入。

圖 5所示是一整體的結構。 由圖上可看出 ICAP-AES分析儀器各部分的相關配置及功能的相關作用。

圖 5　ICP-AES光譜儀的組合圖示



討　　論

張愛華問：

AB-DTPA 法因不穩定故其試藥需當天配，應如何做較適宜?

楊光盛答：

1. 可將單獨之藥品配好，要用時再將各藥品混合，調整 pH 爲 7.6 即可。
2. 目前所分析之土壤樣本中，pH > 7.5 者不多，故無需預先配製。

邱再發問:

ICP 之耗資爲每個月 42 萬，是否對全部費用而言？是否收費?

楊光盛答:

1. ICP 每月耗資 42萬是爲全部費用，包括人事，儀器折舊及藥品費；每個樣本之花費在 350 元左右。
2. 目前對外服務需收費，但農民經由本公司各營業所採樣送檢則不收費。